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HIGH-TEMPERATURE INORGANIC GLASS TEXTOLITES

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The properties of glass textolites based on inorganic aluminum phosphate binders and glass fillers with different structures are investigated. The mechanical and dielectric properties of the glass textolites STAF based on silica, glass and basalt fillers as well as lightweight glass textolites filled with microspheres are presented. Glass textolites based on inorganic aluminum phosphate binder can be used to fabricate construction and radiometric articles which operate for prolonged periods of time at high temperatures.

Key words: glass textolites, aluminum phosphate binders, mechanical characteristics, dielectric properties.

In recent years, as the speed and duration of long-distance flights have increased, new problems associated with the appearance of significant mechanical loads on materials, prolonged aerodynamic heating (to 900°C and higher) and erosion due to external factors have arisen. It is not always possible to use metallic materials under these conditions, specifically, in the preparation of radioparent and heat-shielding structural elements.

The glass textolites currently used for such purposes in aerospace technology, which are based on organic and elemental organic matrices, can operate only to temperature 400°C [1 – 6]. Ordinarily, ceramic-based materials are used to produce articles operating for a long time (hours) at high temperatures (> 1000°C) [7].

In Russia and other countries glass-crystal materials (sitals) obtained by high-temperature firing are used to fabricate heat-resistant radioparent structures, for example, nose cones [8]. Ceramic nose cones require the use of time-consuming methods of centrifugal casting and direct pressing under high pressures. However, ceramic materials cannot always be used for large fairings because of technological difficulties and high cost. Here, one of the difficult problems is to secure the bonding of a ceramic material to metal: high stresses appear because the CLTE of the materials at the bonding sites is different, which leads to material failure.

The need for materials that operate at higher temperatures has stimulated the development of glass textolites based on inorganic matrices, specifically, phosphate binders [9].

An alternative to ceramic materials could be high-temperature glass textolites based on inorganic aluminum phosphate and aluminum-chromium phosphate binders.

Aluminum phosphate binders are widely used in industry, for example, in the porcelain and earthenware industry for mounting the bottom slab and framework of stackable tunnel trolleys, which increases the service life six-fold, in the glass industry to secure the heat insulation of glass-making furnaces so as to prevent the molten glass from penetrating through the brickwork and in other applications.

Glues with high mechanical strength and heat resistance have been developed on the basis of aluminum phosphate binders. In addition, aluminum phosphate glues do not emit gaseous products during heat treatment, and for this reason they are used to secure the interior parts of vacuum apparatus and setups.

B. A. Kudishina, V. T. Minakov, and N. A. Rozdina at VIAM have developed a modified aluminum-phosphate binder SAFS which was used as a base for work on the development of composites and glues.

Being a crystal-chemical analog of quartz this compound undergoes polymorphic transformations similar to those of SiO_2. The modification transformations of quartz are accompanied by significant volume changes, which can result in falls because these cements are prone to cracking and possess a series of other drawbacks [10]. This made it necessary to search for ways to increase their strength.

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The search was conducted in two ways: synthesis of phosphate binders with a different chemical composition and strengthening of the matrix with different reinforcing fillers.

One variant for increasing the strength of materials based on aluminum phosphate binders is reinforcement with different glass fillers. Work on the development of such materials (glass textolites ‘STAF’) was started at VIAM under the direction of Doctor of Technical Sciences B. A. Kiselev (V. N. Bruevich, L. G. Sharova, and S. P. Eliseeva participated in this work).

Initially, the strength of the new material was low because of thermal softening of the glass-fiber filler and its destruction as a result of corrosion by the phosphoric acid in the binder. Research revealed the critical problems of the technology on which the main efforts must be concentrated during the work on the development of lightweight structures of reliable inorganic glass textolites. These comprise small-diameter fibers which are mechanically stable at temperatures above 400°C, coatings resistant to oxidation, methods for protection and securing mechanical stability of the matrix. It was necessary to develop viscous reaction-barrier coatings on a fiber which provide a diffusion barrier for limiting the interaction of the matrix with the fiber and intermediate layers and removing stresses due to the difference of the CLTE of the matrix and fiber.

These drawbacks of STAF glass textolites based on an aluminum phosphate matrix were largely eliminated by using glass fabrics with special inorganic coatings (STAF-1 glass textolite) and a combined inorganic and polymer coating (STAF-2 glass textolite).

The glass textolites STAF-1 and -2 are composite materials obtained by hot pressing of silica glass fabric KT-11-S8/3-TO-OP1, permeated with a modified aluminum phosphate composition (APC) based on the SAFS aluminum phosphate binder with powdered fillers — fused quartz, aluminum oxide and others.

The technological process for producing glass textolites includes the following operations: preparation of the composite APC, its deposition on glass fabric, drying the glass fabric, package assembly, pressing and heat-treatment.

The composite is deposited on a protected glass fabric KT-11-S8/3-TO-OP1 manually or using a permeation machine. The fabric with the deposited layer of binder is dried at room temperature for 50 – 70 min and then finish dried at 70°C in a heating cabinet. The assembled package-blank is placed in a press and is shaped in a prescribed regime with final solidification temperature 275°C in 2 h. The pressed glass textolites is subjected to additional heat treatment at 400°C for 2 h.

Electron-microscopic studies confirmed the effectiveness of an inorganic coating to protect the fibers from chemically aggressive binders at high temperatures.

The properties of glass textolites based on aluminum phosphate binder are presented in Table 1.

TABLE 1. Properties of the Glass Textolites STAF-1 and STAF-2

Index	Material grade	
	STAF-1	STAF-2
Strength in compression, MPa:		
20°C	24.5	75.0
600°C*	52.5	91.0
Strength in tension, MPa:		
20°C	19.0	30.5
600°C*	41.5	54.5
Strength in bending, MPa:		
20°C	45.0	80.0
600°C*	73.0	100.0
Permittivity, 10^{10} Hz		
20°C	3.51	3.40
800°C	3.12	3.43
Dielectric loss tangent, 10^{10} Hz:		
20°C	0.011	0.015
800°C	0.018	0.023

* After soaking for 200 h.

In the initial state the glass textolites STAF-1 and -2 based on aluminum phosphate binders have relatively low strength, which increases considerably at high temperatures. The density of inorganic glass textolites fluctuates in the range 1650 – 1700 kg/m^3; the thermophysical properties are stable at high temperatures and the dielectric properties are preserved at high temperature and in a wet medium.

The STAF-1 and -2 glass textolites are used at temperatures from –130 to +700°C (heating of the materials to temperature 900°C and higher is admissible), STAF-2 having higher characteristics at the working temperature.

The glass textolites STAF-3 and the basalt plastic STAF-4 were developed on the basis of reinforcing fillers of new structures and a modified aluminum phosphate composition.

The glass fabric T-44(VMP)-T0-OP1 based on VMP high-strength glass with a protective coating is used as the reinforcing filler in the glass textolites STAF-3. The basalt plastic STAF-4 is based on the BT-13 grade basalt fabric and the modified aluminum phosphate composition APC.

The properties of aluminum phosphate materials based on the new reinforcing fillers are presented in Table 2.

The advantages of STAF-3 glass textolite over STAF-1 and -2 are high working temperature and long service life, higher mechanical strength and the possibility of fabricating articles with a complex configuration, including double curvature.

Among the advantages of STAF-4 basalt plastic over other grades of STAF-type glass textolites are a reduction of the cost of the material due to the elimination of a double inorganic coating on the basalt fabric and lower density. The STAF-4 basalt plastic is used to fabricate parts for construc-

TABLE 2. Properties of the glass textolites STAF-3 and Basalt Plastic STAF-4

Index	Material grade	
	STAF-3	STAF-4
Density, kg/m^3	1800 – 1850	1500 – 1550
Strength in compression, MPa:		
20°C	76.0	32.0
600°C*	90.0	45.0
Strength in tension, MPa:		
20°C	47.0	27.05
600°C*	65.0	25.0
Strength in bending, MPa:		
20°C	100.0	52.0
600°C*	130.0	60.0
Elastic modulus in tension, MPa:		
20°C	3800	2300
600°C*	4200	3500

* After soaking for 200 h.

TABLE 3. Properties of STAF-O Glass Textolite

Index	STAF-O	
	Glass microspheres	Sol microspheres
Density, kg/m^3	1350 – 1400	1400 – 1450
Strength in tension, MPa:		
20°C	16.0	36.0
600°C	22.0	42.0
Strength in bending, MPa:		
20°C	52.0	60.0
600°C	65.0	75.0
Strength in compression, MPa:		
20°C	Not determined	53.0
600°C	Same	65.0
Permittivity, 10^{10} Hz		
20°C	″	3.89
600°C	″	3.80
Dielectric loss tangent, 10^{10} Hz:		
20°C	″	0.009
600°C	″	0.007

tion and heat insulation, including with double curvature. The material can be used at temperature 600°C for a long time.

In terms of structure and resistance to prolonged exposure to high temperatures the materials based on aluminum phosphate binder correspond more to a ceramic material. At the same time articles are manufactured from them by a simpler and more accessible technology, similar to the manufacture of composite materials based on polymer binders, which do not require high-temperature firing. Compared with ceramic materials they have a lower density and greater strength in tension and impact toughness, as a result of which they are easily machined by diamond and hard-alloy tools.

The STAF glass textolites based on diamond phosphate binder have good dielectric properties, which do not change much with temperature to 800°C. This makes it possible to recommend such materials for the manufacture of radioparent structures, including large antenna fairings. In addition, articles of different shapes (flattened, triangular, spherical and others) can be fabricated, which is difficult to do with ceramic materials.

To obtain high-temperature materials with low density and thermal conductivity lightweight aluminum phosphate materials based on the APC composite with MC-49 grade glass microspheres or sol microspheres (manufactured from industrial ash wastes) were added as filler.

The initial, lightweight, intermediate sheet materials STAF-O are syntactic prepregs, consisting of a mixture of microspheres in an aluminum phosphate composite deposited on a substrate. The glass fabric KT-11-S8/3-TO-OP1 with a protective coating is used as the substrate. Solidified glass textolites STAF-O are layered materials consisting of alternating layers of single-layer glass textolites and layers of spheroplastic. The characteristics of lightweight STAF-O glass textolites based on glass and sol microspheres are presented in Table 3.

The technology for fabricating STAG-O glass textolite with microspheres of different compositions as filler is similar to that used for glass textolites based on aluminum phosphate binders. The density of glass textolites STAF-O is 15% lower than that of STAF-1, STAF-2 and STAF-3.

The STAF materials based on inorganic binders are recommended for manufacturing articles used in radio engineering and construction, operating at temperature to 900°C. At present these materials are used in aerospace engineering for high-temperature radioparent inserts and for lining of pipes and furnaces in thermal electric power plants.

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